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COATING OF SUBSTRATES

[0001] The invention is directed to a coated workpiece which has improved thermal endurance, and it also relates to providing a method for the production thereof.

[0002] In plant construction, there is a growing demand for workpieces having high thermal endurance. In engines, exhaust-gas units, as well as in gas turbines, e.g. in an airplane gas turbine, very high temperatures in a range of from 500 to 1000°C arise in some areas. On the one hand, component parts employed in such areas are exposed to high mechanical stress and, on the other hand, to high thermal load as a result of the high temperatures that are present. In particular, there is a problem in that such component parts are cooled back to ambient temperature when switching off the engine or turbine. Thereafter, rapid heating occurs when restarting the engine or turbine. This cycle of heating and cooling of component parts represents a specific stress, and only specially equipped workpieces are capable of withstanding such stress.

[0003] One problematic aspect is that materials such as titanium or titanium alloys, which have low density in combination with high strength, as well as mechanical load capacity, show temperature resistance to only a certain extent. In case of the above-mentioned titanium and titanium alloys, the maximum temperature where no impairment of the workpiece occurs is about 500°C. If the temperature exceeds this value, oxidation of the workpiece made of titanium or titanium alloy takes place, and the workpiece becomes unusable.

[0004] Such oxidative degradation not only occurs in titanium or titanium alloys, but also in any other workpieces made of e.g. chromium-nickel steel,

chromium-nickel alloy or nickel-based alloy. It is only the temperature of beginning oxidation that is different.

[0005] Thus, great efforts have been made to improve the thermal endurance of workpieces. One option is to deposit a layer on such a workpiece. In the event of titanium or titanium alloys, layers of aluminum were found useful. However, depending on the base workpiece used, there is also the option of coating another specific layer increasing the temperature resistance of the workpiece. Also, ceramic layers can be used which, however, give rise to very high brittleness, thus ensuring only moderate mechanical load capacity of the surface at high temperatures.

[0006] With titanium, coating of aluminum layers on the titanium material has been found useful. In this case, the aluminum layer coated on the titanium workpiece is heated at a temperature allowing to obtain an intermetallic phase comprising the aluminum layer originally present and the underlying workpiece of titanium or titanium alloy. This alloy layer shows an increased temperature resistance of about 650 to 700°C. As the surface layer thus formed is very hard and brittle, mechanical deformation of such a workpiece in a subsequent treatment step is not possible. There would be immediate damage of the temperature-stable surface layer.

[0007] WO 02/058923 suggests coating an aluminum layer on a titanium sheet by means of roll-bonding. In such roll-bonding, a thin aluminum foil is coated on a titanium sheet or a titanium foil at an elevated temperature of about 500 °C. Owing to the high processing temperatures, the aluminum layer adheres on the titanium sheet. Thereafter, the titanium sheet thus treated can be used to produce shaped articles that are thermally treated in a subsequent processing step. As a result of such thermal treatment, a corrosion-protecting layer consisting of a titanium/aluminum alloy is formed which is converted into a titanium-aluminum mixed oxide layer by exposing the surface layer to oxygen. The method described in WO 02/058923 suffers from the drawback that in those cases where the titanium sheet is

to be provided with an aluminum layer on both sides, this aluminum layer actually has to be coated on both sides of the titanium sheet. This necessitates a very high operative input because either a second station must be present in the roll-bonding unit, allowing coating of a second aluminum layer, or the titanium sheet has to be passed twice through the roll-bonding unit. Another drawback of the method described above is that only metal sheets or foils can be provided with an aluminum layer in order to subsequently produce shaped component parts from these metal sheets. Providing a workpiece of three-dimensional design with an aluminum layer by roll-bonding is not possible.

[0008] Another method of surface finishing of titanium workpieces has been described in DE 41 12 218. A titanium substrate is coated with a layer having the composition MCrAl or MCr, wherein M is a metal selected from the group of iron, nickel, cobalt and mixtures thereof. These alloys are coated on the titanium substrate using highly complex processes such as plasma spraying, chemical vapor deposition or physical vapor deposition. In particular, with workpieces of angular shape, these methods have been found to provide only a thin metal layer in areas difficult to access. Consequently, the surface layer is particularly thin in those areas which are to ensure temperature stability of the workpiece. Another drawback is that the above-mentioned coating procedures, such as plasma spraying, chemical vapor deposition or physical vapor deposition, can only be carried out with relatively small workpieces, because the reaction chambers required for this purpose usually can accommodate relatively small workpieces only. These methods have been found unsuitable in those cases where larger workpieces are to be treated.

[0009] The object of the present invention is therefore to overcome the disadvantages of the prior art. More specifically, the technical object of the present invention is to provide a coated workpiece having superior high-temperature resistance and a method for the production of such coated workpieces. In particular, geometrically complex and large workpieces are to be provided with a protective

layer homogeneously distributed on the workpiece. The method used to this end should be easier to carry out and more favorable in cost.

[0010] The technical object of the present invention is accomplished by means of a method for the production of coated workpieces, comprising the steps of:

a) electrodeposition of one or more layers containing at least one metal and/or metal alloy on a substrate, and

b) thermal treatment of the coated substrate at a temperature of between 300°C and 1000°C in such a way that at least the surface layer of the substrate and the layer or layers applied in step a) partially and/or completely interdiffuse.

[0011] In a preferred embodiment the substrate of step a) is electrically conductive. In a likewise preferred fashion the substrate of step a) is a metallic substrate and/or a metallized substrate. The metallic substrate and/or metallized substrate can include one or more metals, said metals preferably being transition metals.

[0012] The substrate is preferably selected from the group of substrates including the metals magnesium, zinc, tin, titanium, iron, nickel, chromium, vanadium, tungsten, molybdenum, manganese, cobalt and mixtures and/or alloys thereof. Preferred substrates are substrates including titanium, titanium alloys, chromium-nickel steel, chromium-nickel alloys and/or nickel-based alloys.

[0013] The electrodeposition of the layer/layers of step a) can be effected using any electroplating method known to those skilled in the art. More specifically, the layer coated in step a) can be coated from a non-aqueous electrolyte or from an aqueous electrolyte.

[0014] The layer of step a) is preferably selected from aluminum, magnesium, tin and mixtures and/or alloys thereof. In a preferred fashion the layer includes an aluminum/magnesium alloy and/or an aluminum/tin alloy.

[0015] When two or more electrodeposited layers of step a) are present, the first layer coated on the substrate (intermediate layer) preferably includes metals selected from the group of iron, iron and nickel, tin and nickel, nickel, cobalt, copper, chromium, molybdenum, vanadium or alloys of the above-mentioned metals. It is possible to coat one or more intermediate layers on the substrate. Thereafter, the intermediate layer is coated with an outer layer selected from aluminum, magnesium, tin and mixtures and/or alloys thereof. The outer layer preferably includes an aluminum/magnesium alloy and/or an aluminum/tin alloy.

[0016] In those cases where the layer or the outer layers of a layer structure include an aluminum/magnesium alloy, the layers preferably include 1 to 80 wt.-% magnesium, more preferably 2 to 50 wt.-% magnesium, even more preferably 3 to 40 wt.-% magnesium, and most preferably 4 to 30 wt.-% magnesium.

[0017] In those cases where the layer or the outer layers of a layer structure include an aluminum/tin alloy, the layers preferably include 1 to 80 wt.-% tin, more preferably 2 to 50 wt.-% tin, even more preferably 3 to 30 wt.-% tin, and most preferably 4 to 25 wt.-% tin.

[0018] Each layer coated in step a) preferably has a layer thickness of from 0.1 μm to 100 μm. In another preferred embodiment the layer thickness is from 0.5 μm to 70 μm, more preferably from 1 μm to 50 μm, preferably from 2 μm to 40 μm, more preferably from 3 μm to 30 μm, even more preferably from 4 μm to 28 μm, and most preferably from 5 μm to 25 μm.

[0019] In those cases where the layer or one of the layers of step a) is electrodeposited from an aqueous electrolyte, solutions of the above-mentioned metals can be used as possible electrolytes. More specifically, the metals can be present in the form of halides, sulfates, sulfonates or fluoborates. The electrolytes may contain further additives such as complexing substances.

[0020] In those cases where the layer or one of the layers of step a) is electrodeposited from an non-aqueous electrolyte, it is possible to use all non-aqueous electrolytes known to those skilled in the art. Possible electrolytes include compounds of the above-mentioned metals. The metals are preferably in the form of halides which can be complexed with ether, particularly diethyl ether. However, the metals can also be present as acetylacetonates (acac).

[0021] For a layer, if it is a layer including aluminum/magnesium, aluminum or a layer including aluminum/tin, it is alternatively possible in step a) to use any electrolyte known to those skilled in the art.

[0022] More specifically, the electrolyte preferably includes organoaluminum compounds of general formulas (I) and (II):

$M[(R^1)_3Al\text{-}(H\text{-}Al(R^2)_2)_n\text{-}R^3]$ (I)

$Al(R^4)_3$ (II)

wherein n is equal to 0 or 1, M is sodium or potassium, and R^1, R^2, R^3, R^4 can be the same or different, R^1, R^2, R^3, R^4 being a C_1-C_4 alkyl group, and a halogen-free, aprotic solvent being used as solvent for the electrolyte.

[0023] A mixture of $K[AlEt_4]$, $Na[AlEt_4]$ complexes and $AlEt_3$ can be employed as electrolyte. The molar ratio of complexes to $AlEt_3$ is preferably from 1:0.5 to 1:3, more preferably 1:2.

[0024] Electrolytic deposition of the layer can be performed using a soluble anode including the metals to be deposited. This anode either can include the metals intended for deposition in the form of a metal alloy, or multiple soluble anodes of the respective pure metals can be used. If a layer including an aluminum/magnesium alloy is to be deposited, it is possible to use a soluble aluminum anode and a likewise soluble magnesium anode or an anode of an aluminum/magnesium alloy.

[0025] Correspondingly, if a layer including an aluminum/tin alloy is to be deposited, it is possible to use a soluble aluminum anode and a likewise soluble tin anode or an anode made of an aluminum/tin alloy.

[0026] Electrolytic coating from a non-aqueous electrolyte is preferably performed at a temperature of from 80 to 105°C. Preferred is an electroplating bath temperature of from 91 to 100°C.

[0027] In a preferred embodiment an electrically conductive layer is coated on the substrate prior to electrodepositing the layer in step a). The electrically conductive layer can be coated on the substrate using any method known to those skilled in the art. In a preferred fashion the electrically conductive layer is coated on the substrate by means of metallization.

[0028] In step b) of the method according to the invention the temperature and/or duration of the thermal treatment is selected in such a way that an alloy containing metal of the surface layer of the substrate and metal and/or metal alloy of the coated layer will be formed at least in the boundary area between substrate and coated layer of step a). Here, temperature and/or duration of the thermal treatment

must be selected in a way so as to be adjusted to the properties of the substrate and to the specific layer being coated.

[0029] In principle, the conditions can be selected such that the coated substrate is treated below the melting temperature of the layer coated in step a). In the event of a layer including aluminum or an aluminum alloy, this temperature preferably is < 650°C.

[0030] As a result of such heat treatment, an intermetallic phase will generally form on the surface of the coated workpiece, wherein the layer coated in step a) is converted either partially or completely into the intermetallic phase.

[0031] Alternatively, the coated substrate can be annealed below/along the liquidus line of the material mixture being formed. The liquidus line is the melting temperature of the resulting material mixture as a function of the specific composition. When coating an aluminum layer on a titanium substrate, the initial proportion of aluminum in the surface layer will be 100%. During heat treatment, a titanium/aluminum alloy is formed which has a specific melting point. Now, when selecting the temperature during heat treatment in a way so as to precisely reach or fall just below the melting point of the alloy being formed, such heat treatment is understood to be heat treatment below/along the liquidus line of the material mixture being formed.

[0032] Alternatively, the heat treatment of the coated substrate can be carried out in such a way that a liquid phase will form on the surface of the coated substrate. This is achieved by performing the treatment at a temperature which is higher than the melting temperature of the surface layer being formed.

[0033] Heat treatment can be effected under a protective gas atmosphere. In this context, it is preferred to use a protective gas that would not undergo

reaction with the coated material. Preferably, the protective gas is a noble gas such as argon. However, it is not necessary that heat treatment be performed in a protective gas atmosphere. Alternatively, heat treatment can also be effected in air.

[0034] The temperature of thermal treatment of step b) is preferably between 400°C and 1000°C, more preferably between 450°C and 900°C, and most preferably between 500°C and 800°C.

[0035] The duration of heat treatment in step b) can be between one second and 10 hours and is preferably between 1 minute and 5 hours and most preferably between 2 minutes and 3 hours. Alternatively, the thermal treatment in step b) can be effected after the workpiece has been mounted in its intended place. In this way, e.g. an engine element or turbine element can be heated during its first use in such a way that the surface layer of the substrate undergoes diffusion with the coated layer.

[0036] Subsequent to coating the layer in step a) and prior to performing the heat treatment of step b), the layer is subjected to further treatment in a preferred embodiment. Any treatment procedure known to those skilled in the art can be used. In particular, the treatment can be anodic oxidation, preferably anodization of the layer. Such treatment is recommendable in those cases where a layer including aluminum has been coated in step a).

[0037] The coated workpieces employed in the method of the present invention are preferably rack goods, bulk materials, continuous products or molded articles. The coated workpiece is preferably a wire, a metal sheet, a screw, a nut, a concrete anchorage, a machine component part, an engine, an engine part, or a turbine blade.

[0038] The workpieces produced according to the method of the present invention have outstanding long-term resistance to thermal load. In repeated cycles of heating and cooling the workpieces do not exhibit any corrosion due to thermal load over a long period of time. In particular, the coated workpieces show improved resistance to oxidation or other corrosive high-temperature effects where the uncoated workpiece, i.e., the substrate, would already begin to corrode.

[0039] In the event of an uncoated substrate containing titanium or a titanium alloy, permanent damage as a result of oxidation can already be seen at 650 °C. In contrast, a coated titanium substrate in accordance with the present invention, e.g. coated with aluminum or with an aluminum/magnesium alloy, exhibits temperature stability in a range of 750 to 1000°C.

[0040] The coated substrates of the present invention are significantly more temperature-resistant compared to those of the prior art. Without intending to be bound by any theory, one explanation might be that highly pure layers are obtained by such electroplating, while in prior art coating methods, e.g. chemical vacuum deposition, physical vacuum deposition or plasma spraying, impurities are present in the coated layers, adversely affecting the thermal stability. Since electroplating furnishes high-purity layers, seeds caused by impurities are absent in such layers. As a consequence, highly pure diffusion layers are formed which, as a result of said high purity, exhibit improved stability, particularly improved thermal stability.

[0041] Another drawback is that the above-mentioned methods of the prior art can barely be used for coating a layer on geometrically complex substrates. Specifically in corners and edges, the layer thickness is lower than that on easier accessible surfaces. As a result, no homogeneous layer will be formed on the substrate, inevitably giving rise to deteriorated corrosion resistance in those areas where the layer thickness is lower. As a result of electrodepositing the layer on the substrate, a homogeneous layer of sufficient thickness is formed even in areas diffi-

cult to access, e.g. in corners and edges. Thus, the diffusion layer obtained by thermal treatment has sufficient layer thickness and, as a consequence, sufficient and improved corrosion stability even in those areas difficult to access due to their geometry. Especially in this respect, the workpieces obtained by means of the present invention are different from the prior art workpieces. Further, as a result of coating high-purity layers, highly pure diffusion layers are formed even in such critical areas upon thermal treatment, as set forth above.

[0042] Another advantage of the method of the present invention is its lower cost compared to methods of the prior art. Electrodeposition of a layer is more economical than e.g. plasma spraying. Another advantage can be seen in the fact that the thermal load on the substrate is higher in plasma spraying as well as in e.g. chemical vacuum deposition or physical vacuum deposition. Particularly with geometrically complex substrates, this gives rise to thermal distortion of the workpiece. When using the method of the present invention, the thermal load on the workpiece in step a) is significantly lower. In this way, it is possible to produce coated workpieces with lower production tolerances, resulting in substantial advantages in subsequent operation, e.g. as a turbine blade. Furthermore, lower production tolerances in coated workpieces with high thermal load provide a higher level of safety. Workpieces produced by means of the method of the present invention, e.g. turbine blades, when mounted in a gas turbine, ensure wider safety margins compared to turbine blades of the prior art.

[0043] Without intending to be limiting, the invention will be explained with reference to the following examples.

Examples

1. Coating a substrate

[0044] A titanium sheet 5 × 25 × 1 mm in size is provided with a layer of aluminum having a layer thickness of 12 μm, using electrodeposition from a non-aqueous electrolyte.

2. Thermal treatment of the metal sheet

[0045] The titanium sheet provided with a layer of aluminum is heated in an oven to the temperature indicated in Table 1. The temperature is maintained for the time period indicated in Table 1. Thereafter, the coated titanium sheet is removed from the oven and cooled in an air atmosphere. During the process of alloying, the oven is supplied with ambient air or argon protective gas.

Table 1

Number	Heating rate	Temperature	Holding time	Cooling	Atmos-phere
A	Rapid	700°C	5 min	Air	Ambient
B	Rapid	700°C	5 min	Air	Argon
C	Slow	650°C	30 min	Air	Argon

3. Determination of corrosion resistance to elevated temperature.

[0046] The coated titanium sheets numbered A, B and C are heated in an oven to the temperature indicated in Table 2. After the holding time indicated in Table 2, the material samples are removed from the oven, cooled, and the corrosion

of the coated titanium is assessed visually. As can be seen, the coated layer results in outstanding corrosion resistance even at very high temperatures, e.g. 900°C. A non-coated titanium sheet would suffer permanent damage by oxidation at a temperature from 650°C on. Even at a holding time of 384 hours at 700°C, there is no noticeable corrosion of the coated titanium sheet.

Table 2

	1.5 h	24 h	48 h	96 h	192 h	384 h
650°C		OK				
700°C		OK	OK	OK	OK	OK
750°C		OK	OK	OK	OK	
800°C	OK	OK	OK	OK	OK	
900°C		OK				

[0047] In summary, it can be seen that a titanium sheet produced according to the method of the present invention has improved corrosion resistance. The workpieces thus coated are significantly more resistant to corrosion than prior art workpieces. In particular, the corrosion resistance at elevated temperatures is markedly improved.